Do cover crops enhance N_2O, CO_2 or CH_4 emissions from soil in Mediterranean arable systems?

A. Sanz-Cobena , S. García-Marco , M. Quemada , J.L. Gabriel , P. Almendros , A. Vallejo

Keywords:
Cover crops
GHG emissions
Green manure
Irrigation
Maize

A B S T R A C T

This study evaluates the effect of planting three cover crops (CCs) (barley, *Hordeum vulgare* L.; vetch, *Vicia villosa* L.; rape, *Brassica napus* L.) on the direct emission of N_2O, CO_2 and CH_4 in the intercrop period and the impact of incorporating these CCs on the emission of greenhouse gas (GHG) from the forthcoming irrigated maize (*Zea mays* L.) crop. Vetch and barley were the CCs with the highest N_2O and CO_2 losses (75 and 47% increase compared with the control, respectively) in the fallow period. In all cases, fluxes of N_2O were increased through N fertilization and the incorporation of barley and rape residues (40 and 17% increase, respectively). The combination of a high C:N ratio with the addition of an external source of mineral N increased the fluxes of N_2O compared with −Ba and −Rp. The direct emissions of N_2O were lower than expected for a fertilized crop (0.10% emission factor, EF) compared with other studies and the IPCC EF. These results are believed to be associated with a decreased NO_3^- pool due to highly denitrifying conditions and increased drainage. The fluxes of CO_2 were in the range of other fertilized crops (i.e., 1118.71–1736.52 kg CO_2–C ha^{-1}). The incorporation of CC residues enhanced soil respiration in the range of 21–28% for barley and rape although no significant differences between treatments were detected. Negative CH_4 fluxes were measured and displayed an overall sink effect for all incorporated CC (mean values of −0.12 and −0.10 kg CH_4–C ha^{-1} for plots with and without incorporated CCs, respectively).

1. Introduction

Agricultural soils are assumed to be one of the major sources of greenhouse gases (GHGs), particularly nitrous oxide (N_2O) and methane (CH_4) (OECD, 2000; IPCC, 2007). Several agricultural practices (e.g., nitrogen fertilization, irrigation, residues management) have been shown to be driving variables in the emission of these gases within the crop period (IPCC, 2007). However, some of these management practices can also affect emissions in the fallow period, especially when the nitrogen (N) use efficiency (NUE) of the crops is low and, therefore, large amounts of mineral N (as residual N) remain in the soil after harvest (Sanchez-Martín et al., 2010).

In Mediterranean areas, intensively irrigated and fertilized systems normally present high levels of mineral N, which tends to be lost through leaching and/or denitrification during both the cropping and fallow periods (Gabriel and Quemada, 2011; Sanz-Cobena et al., 2012; Aguilera et al., 2013). Therefore, replacing bare fallow with cover crops (CCs) has been proposed as an agricultural technique to increase the retention of post-harvest surplus inorganic N and to reduce nitrate leaching (Dinnes et al., 2002). Based on this, different types of winter CCs have been used as catch crops under Mediterranean conditions (Gabriel and Quemada, 2011). However, due to the N and water demand of these crops, changes in soil moisture and N and C pools

may occur in the CC period, thus influencing the processes leading to the emission of GHGs.

The type and characteristics of these crops (e.g., root depth, N and water demand, release of nutrients in the rhizosphere, adaptation to climatic conditions) are key factors related to improving NUE in the system (Gabriel and Quemada, 2011). In this sense, cereals often decrease the soil N content at early growth stages due to a higher N uptake and decreased drained water, both associated with a faster initial rooting (Thorup-Kristensen et al., 2003). Crucifers have a superior N uptake capacity at later growth stages and a deeper rooting system, allowing them to recover N more efficiently from deeper zones (Thorup-Kristensen et al., 2003). Legumes have also been evaluated as catch crops (Pappa et al., 2011), and it has been demonstrated that 50–60% of the N in their tissues comes directly from N uptake (Gabriel and Quemada, 2011). Although all these changes in soil conditions could affect GHGs in the CC period, to date, there is only limited and highly specific information regarding both CC species (i.e., legumes) and climatic area (i.e., temperate) on the effect of CCs on GHG emission (e.g., Baggs et al., 2000; Chirinda et al., 2010; Pappa et al., 2011).

In crop rotations with CCs used as catch crops, the biomass of CCs is frequently used as green manure after harvest to reuse the N retained by CCs, thus contributing to the maintenance of long-term soil fertility in the forthcoming crop (Olesen et al., 2007). In this case, the quality, the N content and the mineralization potential of the plant material, as defined by (e.g.) the C:N ratio, the lignin content and the N_2 fixing capacity, also affect the dynamics of N and C in the soil (Berntsen et al., 2006; Olesen et al., 2007), conditioning GHG emission after their application to soils (Chirinda et al., 2010; Pappa et al., 2011).

The incorporation of crop residues in fertilized soils can increase N_2O emissions from arable soils (e.g., Huang et al., 2004; Frimpong and Baggs, 2010), which are highly dependent on the composition of residue biomass. Generally, residues with low C:N ratios enhance N_2O emission (Huang et al., 2004). In contrast, at high C:N ratios, a temporary reduction on N_2O losses is often produced as a consequence of a temporary N immobilization, which delays the release of N into the soil (Gentile et al., 2008). In a CC–cereal rotation, the availability of N for the main crop (cereal) is affected by the green manure from previous CC and, generally, an additional source of N (i.e., N fertilizer). The combined effect of residues and an external source of N also affect the emission of N_2O. In this context, the combination of mineral N from fertilizer and a residue with a high C:N ratio may promote and increase N_2O and CO_2 emissions in comparison with N fertilizer alone because soluble organic C from residue can be used as an energy source for denitrifiers (Sarkodie-Addo et al., 2003; Abalos et al., 2012).

Although, to our knowledge, there are no studies simultaneously comparing the effect of different types of crops (e.g., legume/cereal/crucifer) on direct GHG emissions under Mediterranean conditions, we hypothesized that replacing bare fallow with cover crops would be a good strategy to reduce the overall GHG emission in the intercrop period during autumn–winter. The adequate selection of CCs, adapted to these climatic conditions, could be a key method used to decrease the pool of mineral N and soil moisture, thus lowering the emission of GHGs. In addition, the incorporation of CC residues with contrasting characteristics would affect the net GHG budget of the cropping system differently. Although the C:N ratio determines the prevalence of N retention (i.e., immobilization) or release (i.e., mineralization) from the residues, and consequently N_2O emission, the application of a N fertilizer could affect GHG fluxes by changing the total C:N ratio and the possible effect of the incorporated residue. Based on this process, we expected higher N_2O fluxes for the cereal CC (higher C:N ratio) than for legumes (lower C:N ratio). In the case of CH_4 emissions, the oxidation of this compound could be affected by the amount of mineral N in the soil (Steudler et al., 1989; Hütsch et al., 1996; Le Mer and Roger, 2001). This could be the case if the pool of mineral N increases as a result of the mineralization of N-rich plant material from legumes used as green manure.

The objectives of this study were 1) to evaluate the effect of three different crop species (legume, cereal and crucifer) used as CCs on the GHG emissions of an intercrop period traditionally left in the region as bare soil and 2) to assess the influence of incorporating the residues of these CCs as green manure on the net GHG balance of the entire system. An additional objective was to determine the relation of N_2O emissions with the crop N uptake and grain yield of maize. Crop-specific-yield scaled GHG emissions may allow us to suggest specific practices, focused on CC management, to abate these losses in irrigated maize systems (van Groenigen et al., 2010).

2. Materials and methods

2.1. Experimental location

The study was conducted for 12 months at the "la Chimenea" field station (40°03′N, 03°31′W, 550 m a.s.l.) located in the central Tajo river basin near Aranjuez (Madrid, Spain). Soil at the field site is a silty clay loam (Typic Calcixerept; soil Survey Staff, 2003), calcareous and rich in organic matter and carbonates. Some of the physico-chemical properties of the top 0–23 cm of the soil layer, as measured by conventional methods, were as follows: pH_{H2O}, 8.23; total organic C, 18.51 g kg^{-1}; bulk density, 1.36 g cm^{-3}; $CaCO_3$, 198 g CO_3^{-2} kg^{-1}; clay, 250 g kg^{-1}; silt, 490 g kg^{-1} and sand, 260 g kg^{-1}. The area has a Mediterranean semiarid climate (Papadakis, 1966) with high interannual variability. The mean annual air temperature in this area is approximately 14 °C. The coldest month is January with a mean temperature of 6 °C, and the hottest month is August with a mean temperature of 24 °C. In the last 30 years, the mean annual precipitation has been approximately 350 mm (17 mm from July to August and 131 mm from September to November).

2.2. Experimental design and cover crop management

Fifteen plots (12 × 12 m) were set in the field, and five cover cropping treatments were used: 1) barley (Ba) (*Hordeum vulgare* L., cv. Vanessa, 180 kg ha^{-1}, ~500 plants m^{-2}), 2) vetch (Vt) (*Vicia villosa* L., cv. Vereda, 150 kg ha^{-1}, ~210 plants m^{-2}), 3) rape (Rp) (*Brassica napus* L., cv. Licapo, 6 kg ha^{-1}, ~170 plants m^{-2}), 4) traditional fallow (F) and 5) bare fallow without N fertilization in the previous 4 years as a control soil (fallow control, FC). The plots and treatments were arranged in a fully randomized design with three replicates. Cover crops were broadcasted by hand over maize stubble and covered with a shallow cultivator (depth of ~5 cm) on October 5, 2009, and received one application of glyphosate 2% (N-phosphonomethyl glycine) on March 18, 2010. On April 12, all the CC residues were incorporated into the soil in half of each plot and chopped straw was left on top of the soil in the other half. Thereafter, a new set of treatments was set up. These were soil with incorporated residues from barley, vetch and rape (i.e., +Ba, +Vt and +Rp) and soils without CC residues incorporated (i.e., −Ba, −Vt and −Rp). The main characteristics of the residues are shown in Table 1. Maize (*Zea mays* L., G-98 Pioneer, FAO Class 700) was sown in all treatments, resulting in a plant population density of 7.50 plants m^{-2} on April 13, 2010, and harvested on October 7, 2010 (Fig. 1). Irrigation of the maize crop was applied at a total rate of 760 mm. Each plot received 120 kg ha^{-1} of P as triple superphosphate (45% P_2O_5, Fertiberia®, Madrid, Spain) and K as potassium sulfate (50% K_2O, Fertiberia®, Madrid, Spain) before the sowing of maize, and in all cases but the FC, 210 kg N ha^{-1} as ammonium nitrate (AN: NH_4NO_3 33.50% N richness from Fertiberia®, Madrid, Spain) was split in two applications (two-thirds on May 27 and one-third on June 29, 2010) and broadcasted over the plots, followed by an irrigation event. This CC and maize rotation was established in the same plots

Table 1
Dry biomass, N uptake, C/N ratio, acid and neutral detergent fibers of cover crops immediately after incorporation in the maize crop and maize grain yield (n = 4 in all the analysis). ADF, ADL and NDF are the acronyms for acid detergent fibers, acid detergent lignin and neutral detergent fibers, respectively.

Cover crop	Dry biomass (kg ha^{-1})	N uptake (kg N ha^{-1})	NDF (%)	ADF (%)	ADL (%)	C/N ratio	Maize grain yield (kg ha^{-1})
Barley	4114.42 ± 647.91	67.31 ± 15.56	43.11 ± 3.50	17.90 ± 1.41	2.30 ± 0.41	19.91 ± 2.20	8017.11 ± 894.89
Rape	2070.27 ± 134.51	56.05 ± 4.45	30.91 ± 2.01	15.63 ± 1.41	4.94 ± 1.26	14.81 ± 0.54	8478.03 ± 503.45
Vetch	1984.29 ± 306.62	55.44 ± 8.44	33.02 ± 4.17	15.35 ± 2.43	4.83 ± 0.91	11.22 ± 0.93	8674.23 ± 639.13

for 4 years preceding this study (see Gabriel and Quemada (2011) for further details on Ba, Vt and F treatments, which are also applicable to Rp and FC as part of a broader study).

2.3. Sampling and analysis of GHG fluxes

Greenhouse gas fluxes were sampled using the closed chamber technique (Clayton et al., 1994). Two opaque and vented manual chambers with a headspace of 19.30 L (diameter 35.60 cm, height 19.30 cm) were placed in each plot. The chambers were closed by fitting them into stainless steel rings, which were inserted into the soil to a depth of 5 cm to minimize the lateral diffusion of gases and avoid the soil disturbance associated with the insertion of the chambers in the soil (Abalos et al., 2012). At the bottom of the chambers, rubber sealing tape was fixed to ensure an airtight seal between the chamber and ring. The rings were placed at the beginning of the intercrop period (October 5th) and were removed only during crop management practices (e.g., cover crop harvest and incorporation). A rubber stopper with a 3-way stopcock was placed in the wall of each chamber to take gas samples. Greenhouse gas measurements were always made with the CC inside the chamber during the intercrop period and between rows in the maize crop. Thus, in the fallow period, the CO_2 fluxes were net CO_2 fluxes (i.e., the sum of plant and soil respiration).

Gas samples (vol. 20 mL) were taken 0, 30 and 60 min after chamber closure from the headspaces of each chamber using 100 mL syringes fitted with 3-way stopcocks and were transferred to 20 mL gas chromatography vials sealed with a gas-tight neoprene septum. The vials were flushed in the field using 80 mL of the gas sample. To minimize any effects of diurnal variation in emissions, as far as possible, the samples were taken at the same time of day (10–12 am) on each occasion. Thermometers were placed inside three randomly selected chambers during the closure period of each measurement to correct the fluxes for temperature.

Concentrations of GHGs in the gas samples were determined by gas chromatography, using an HP-6890 gas chromatograph (GC) equipped with a headspace autoanalyzer (HT3), both from Agilent Technologies (Barcelona, Spain). A more detailed description of the method and the GC columns used for the analysis of GHG samples can be found in Abalos et al. (2012). The accuracy of the gas chromatographic data was 1% or better. Two gas standards comprising a mixture of gases (high standard with 1500 ± 7.50 ppm CO_2, 10 ± 0.25 ppm CH_4 and 2 ± 0.05 ppm N_2O and low standard with 200 ± 1.00 ppm CO_2, 2 ± 0.10 ppm CH_4 and 200 ± 6.00 ppb N_2O) were provided by Carburos Metálicos S.A. and Air Products SA/NV, respectively, and used to determine a standard curve for each gas. The response of the GC was linear within 200–1500 ppm for CO_2 and 2–10 ppm CH_4 and quadratic within 200–2000 ppb for N_2O.

The flux rates of N_2O, CH_4 and CO_2 were calculated from the change in the chamber gas concentration during the 60-minute period in which the chambers were closed. The linearity of gas diffusion into the headspace over this closure period (60 min) had previously been determined, and each flux could be calculated from a single determination at the end of closure by considering the chamber volume and soil surface (Van Cleemput and Boeckx, 2005). The measurements of GHG emissions were made every two weeks during the intercrop period. In the maize crop period, gas samples were taken on a weekly basis before N fertilizer application and 2 days per week during the two weeks following N fertilizer application. Cumulative gas emissions during the experimental period were calculated as proposed by Menéndez et al. (2006), by multiplying the mean flux of two successive determinations by the length of the period between sampling and adding that amount to the previous cumulative total.

The direct N_2O EF was calculated by the equation proposed by Velthof and Mosquera (2011), which is in line with the IPCC method and equates the EF to the difference between the N_2O emitted from fertilized soil and that from the control divided by the N applied within the fertilizer. It must be noted here that the EF and flux discussed in this work are only the direct GHG flux and EF and do not include the indirect portion of any EF or flux:

$$\mathrm{EF}(\%) = \frac{[(N_2O \text{ emission from fertilize soil}) - (N_2O \text{ emission from control})]}{\mathrm{N\,applied}} * 100.$$

2.4. Soil analyses

To relate GHG emissions to soil properties, soil samples were collected from each plot at a 0–20 cm depth using an Eijkelkamp® helicoidal hand auger (vol. 0.07 dm^3). Three samples of soil were randomly collected from each plot and then mixed, thoroughly homogenized and refrigerated at 4 °C for 2 to 4 days until extraction. Within five consecutive days, the samples were extracted and then stored in a freezer until quantitative determination (7–15 days). Soil mineral N

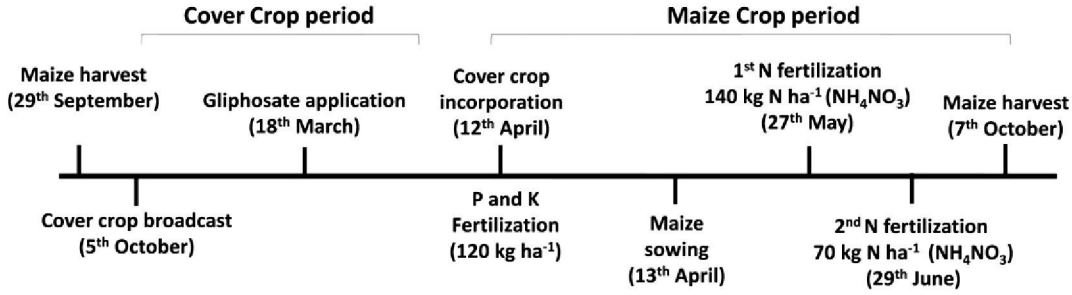

Fig. 1. Chronogram of management practices conducted within the experimental period.

(nitrate, NO_3^- and ammonium, NH_4^+) was extracted with 1 M KCl using a 1:5 soil:extractant ratio. Nitrate was determined by spectrophotometry after reduction to nitrite (NO_2^-) using a cadmium column and NH_4^+ was analyzed using the phenolhypoclorite method. These two methods are included in the ISO/TS, 14256–1: (2003) standard methodology. Dissolved organic carbon (DOC) was extracted with water at 1:5 soil:extractant ratio and analyzed using the permanganate oxidation method described in BOE (1987) as an official method for the physico-chemical analysis of public drinking water in Spain.

Water-filled pore space (WFPS), defined as the % of soil pores full of water, was estimated by dividing the volumetric water content by total soil porosity. Total soil porosity was calculated by measuring the bulk density of the soil according to the following relationship: soil porosity = 1 − (soil bulk density / 2.65), assuming a particle density of 2.65 mg m^{-3} (Danielson and Sutherland, 1986).

Volumetric water content was derived from soil moisture data monitored using four frequency domain reflectometry (FDR) probes (EnviroScan system, Sentek Sensor Technologies, Stepney, SA, Australia) (i.e., one probe per treatment). Each probe consisted of sensors located at depths of 10, 30, 50 and 80 cm inside a thin-walled PVC tube (with an external diameter of 5.60 cm). All sensors were calibrated before the field study by Gabriel et al. (2010). The measurements were made as described in Sanchez-Martin et al. (2010).

Rainfall and air temperature data were collected using a meteorological station located at the experimental site (CR23X micrologger, Campbell Scientific, Shepshed, UK) equipped with a Young® tipping bucket rain gauge (RM Young Company, Michigan, USA). Soil temperature was monitored using a temperature probe inserted 10 cm into the soil. Mean hourly temperature data were stored on a data logger.

2.5. Drainage

Daily drainage (D) at a depth of 0.80 m was calculated by applying the following simplified one-dimensional (vertical) water balance equation for each measurement position (Arregui and Quemada, 2006):

$$D = R + I - \mathrm{ETc} \pm \Delta S$$

where R is the rainfall (mm), I is the irrigation (mm), ETc. is the evapotranspiration (mm) and ΔS is the change in soil water (mm) between depths of 0 and 80 cm. ETc. was estimated using the crop coefficient Kc, which was calculated with crop data from the FAO and the Penman-Monteith model (Allen et al., 1998) based on data provided by a meteorological station located at the experimental site.

2.6. Analysis of crop residues and yield calculation

Four 0.50 m × 0.50 m squares were randomly harvested from each plot before killing the CC by applying glyphosate. The aerial biomass was cut by hand at the soil level, oven dried at 65 °C, weighed and ground to pass through a 1-mm mesh. From these samples, the CC biomass, total C and N content and fibers were determined (Table 1). The total C and N content were analyzed using the Dumas combustion method with a LECO FP-428 elemental analyzer. The neutral and acid detergent fiber methods (Goering and Van Soest, 1970) were used to determine crop residue quality. To minimize the effect of soil contamination, the residual residue weight was calculated on an ash-free weight basis by determining the ash content (550 °C) of a 1 g subsample from each cover crop biomass. For the maize crop, two 10 m central rows in each plot were harvested, at maturity, and weighed in the field after first separating the grain and straw. The crop yield values represent the production of above-ground biomass (i.e., grain and straw) as a dry weight. Total N was measured following the same method used for CC.

2.7. Statistical analysis

All the experiments were conducted with three replicates. Statistical analysis was performed using Statgraphics Plus 5.1 (Manugistics, 2000). The data distribution normality of the GHG fluxes, soil NO_3^-, NH_4^+ and DOC was verified using the Kolmogorov–Smirnov test. In some cases, the data were log-transformed before analysis. The Least Significant Difference (LSD) test was used for multiple comparisons between the means. For non-normally distributed data, the Kruskal–Wallis test was used on non-transformed data to evaluate differences at $P < 0.05$. Schaich–Hamerle's analysis was also conducted as a post hoc test. Linear regression analyses ($P < 0.05$) were performed to determine the relationships between the GHG fluxes and the soil DOC, NH_4^+, NO_3^-, WFPS and drainage.

3. Results

3.1. Cover crop period

3.3.1. Environmental conditions, soil moisture and drainage

The mean soil temperature in the CC period was 10 °C, ranging from 5.42 °C in January to 16.33 °C in October (Fig. 2a). Total rainfall accounted for 382 mm, higher than the 30-year mean of 253 mm, with a minimum and maximum in October (0.71 mm) and December (142 mm), respectively. The mean soil moisture (WFPS) differed between the treatments in the fallow period, ranging between 40 and 56% WFPS for FC and F, respectively. The WFPS was also influenced by the sampling dates. November was the month with the lowest values, as measured in Ba and Rp (30 and 35%, respectively), whereas the highest values were observed in March for F and Vt (61 and 57%, respectively) (Fig. 2b). No significant differences ($P > 0.05$) were found between treatments and sampling dates. The total drained water in this period was 314.71, 301.32, 288.81 and 233.70 mm for F, Vt, Ba and Rp, respectively. Significant differences ($P < 0.05$) were found between all treatments.

3.3.2. Mineral N and DOC

The ammonium concentration was very low, ranging from 0.12 to 1.14 kg NH_4^+–N ha^{-1} (data not shown). The nitrate concentration ranged from 0.61 to 7.38 kg NO_3^-–N ha^{-1} 40 days after sowing (DAS) for FC and Rp, respectively (Fig. 3a). Initially (i.e., 0 DAS), Vt was the CC displaying the highest NO_3^- concentration (6.42 kg NO_3^-–N ha^{-1}). A threefold decrease was measured 35 days later. In contrast, the NO_3^- concentration in the Rp plots increased from 3.21 to 7.42 kg NO_3^-–N ha^{-1} in the same period (Fig. 3a). In general, there was a decreasing trend in the NO_3^- measured in all cases (Fig. 3a). The dissolved organic carbon (DOC) concentration ranged between 4.41 and 13.48 kg C ha^{-1} for Rp and Ba, respectively, both measured 110 and 150 DAS, respectively. The highest DOC concentration in the other CC was measured on the same date (Fig. 3c). The highest mean concentration was measured 150 DAS in CC plots. Both NO_3^- and DOC concentration were negatively correlated with drainage and WFPS ($P < 0.05$).

3.3.3. GHG fluxes

Nitrous oxide emissions were affected by the presence of CC (Fig. 4a). The daily fluxes ranged between 3.43 and −2.71 g N_2O–N ha^{-1} d^{-1}, both measured 3 DAS in Vt and FC, respectively (Fig. 4a). The soil acted as a sink (i.e., negative fluxes) for N_2O at some sampling events. Negative fluxes were measured in 30% of the samplings for Vt and F and 40 and 70% for Rp and Ba, respectively. Vetch was the CC producing the highest cumulative N_2O emissions at the end of this period, followed by F (Table 2). The FC soil displayed an overall N_2O consumption, whereas no cumulative fluxes were detected in the Ba and Rp treatments. Significant differences ($P < 0.05$) were only observed between Vt and the other treatments (Table 2). The daily

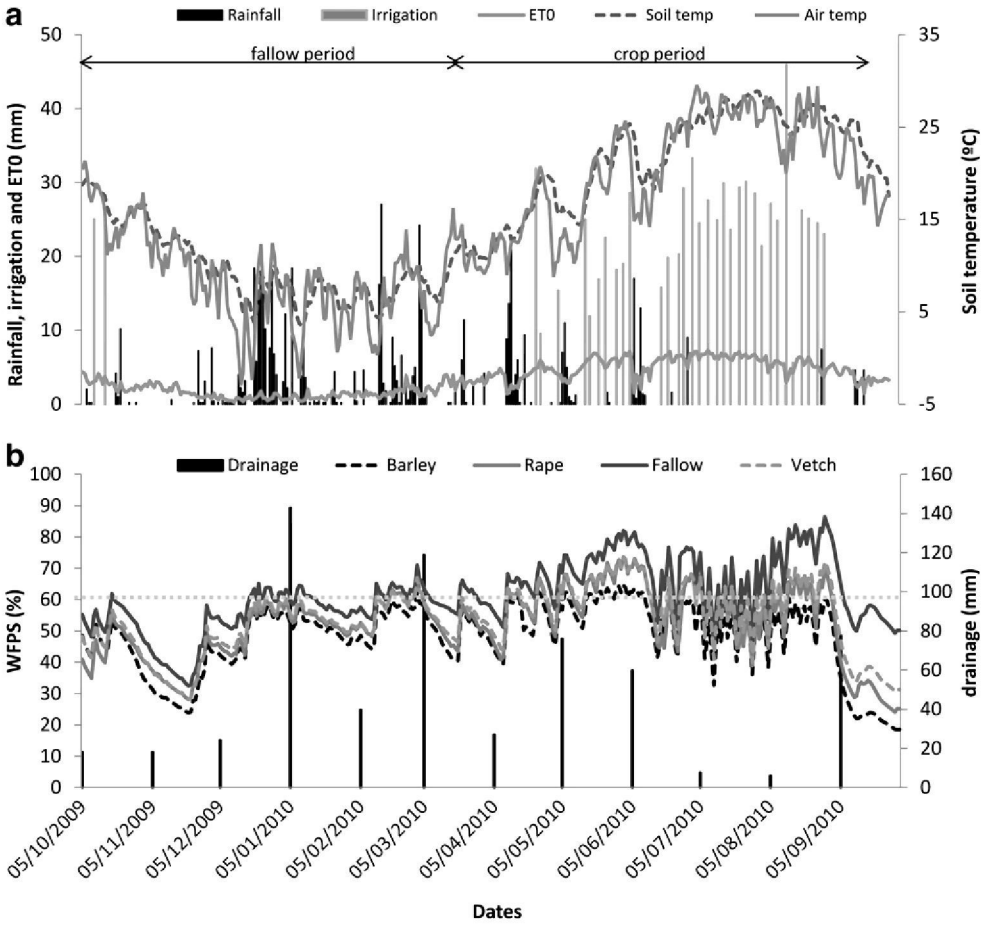

Fig. 2. Daily rainfall (mm), ETo (mm), irrigation (mm) and daily mean soil and air temperature (°C) during the experimental period (a). Soil Moisture content expressed as Water Filled Pore Space (WFPS, %) for the different CCs and maize plots with incorporated CC residues and mean drained water (mm) (n = 3 for each CC) (b). The gray horizontal line indicates the value of 60% WFPS.

fluxes of N_2O were positively and negatively correlated ($P < 0.05$) with NO_3^- and DOC concentration, respectively.

Two peaks of CO_2 were measured in all plots 20 and 100 DAS (October 26 and January 19, respectively). The highest fluxes were observed in Ba and Vt in the first peak, and Ba and Rp in the second one (Fig. 4b). In contrast, the lowest fluxes were measured 15 and 70 DAS and at the end of the CC period. The highest cumulative emissions were observed in the Ba and Vt plots. Significant differences ($P < 0.05$) were observed between Ba and the other treatments and between Vt and FC (Table 2).

The daily fluxes of CH_4 ranged from 6.01 to −14.13 g CH_4–C ha^{-1} d^{-1}, both measured in FC (Fig. 4c). There was an overall sink effect for CH_4 fluxes produced by all CC but Vt (Table 2). No significant ($P > 0.05$) differences were observed among the CH_4 values from the different treatments.

3.4. Maize crop period

3.4.1. Environmental conditions, soil moisture and drainage

The mean soil temperature ranged from 14.22 to 26.81 °C for April and August, respectively. Total rainfall accounted for 151.33 mm, with 94% of that falling in the April–June period (Fig. 2a). Irrigation of maize (760 mm) increased soil moisture compared with the fallow period (Fig. 2b). The F plots managed as plots without incorporated CC (−F), and the −Vt plots displayed the highest WFPS mean values (68 and 58%, respectively). The mean soil moisture in the −Ba and −Rp plots was 50 and 55% WFPS, respectively. Significant differences ($P < 0.05$) were only measured between −F and the three CC plots. The plots with incorporated residues displayed lower WFPS values, averaging 51% in this period. No significant differences ($P > 0.05$) were measured between the plots with and without CC residues. The highest mean soil moisture was measured in May and August (67% WFPS) and the lowest in September (44% WFPS) (Fig. 2b). Irrigation and rainfall did not enhance the volume of drained water compared to the fallow period. No significant ($P > 0.05$) differences were found between plots with incorporated CC. The highest and lowest amounts of drained water were measured in barley and fallow (26 and 216 mm, respectively). The total mean drainage at the end of the experimental period was 526 ± 21 mm, with no significant ($P > 0.05$) differences between treatments.

3.4.2. Mineral N and DOC

The incorporation of green manure from CC did not produce a significant ($P > 0.05$) change in the concentration of NH_4^+. Similar values to the CC period were observed at the beginning of the measurements. NH_4^+ was not higher than 0.72 kg NH_4^+–N ha^{-1} in all plots (data not shown). These values were lower than expected in N fertilized soils, which may suggest that the NH_4^+ peak was missing between our scheduled 1st and 2nd soil samplings. The nitrate concentration increased 20 days after the first fertilization (140 kg N ha^{-1}) (i.e., 60 days after CC residue incorporation and 255 DAS) in all cases (Fig. 3b). Concentrations in the plots where green manures were not incorporated were below 3.71 kg NO_3^-–N ha^{-1} (i.e., 200 DAS) and increased to values higher than 14.74 kg NO_3^-–N ha^{-1} thereafter (255 DAS, Fig. 2b). The 2nd fertilization (70 kg N ha^{-1}) did not increase the NO_3^- pool as much as the 1st fertilization. The nitrate concentrations ranged

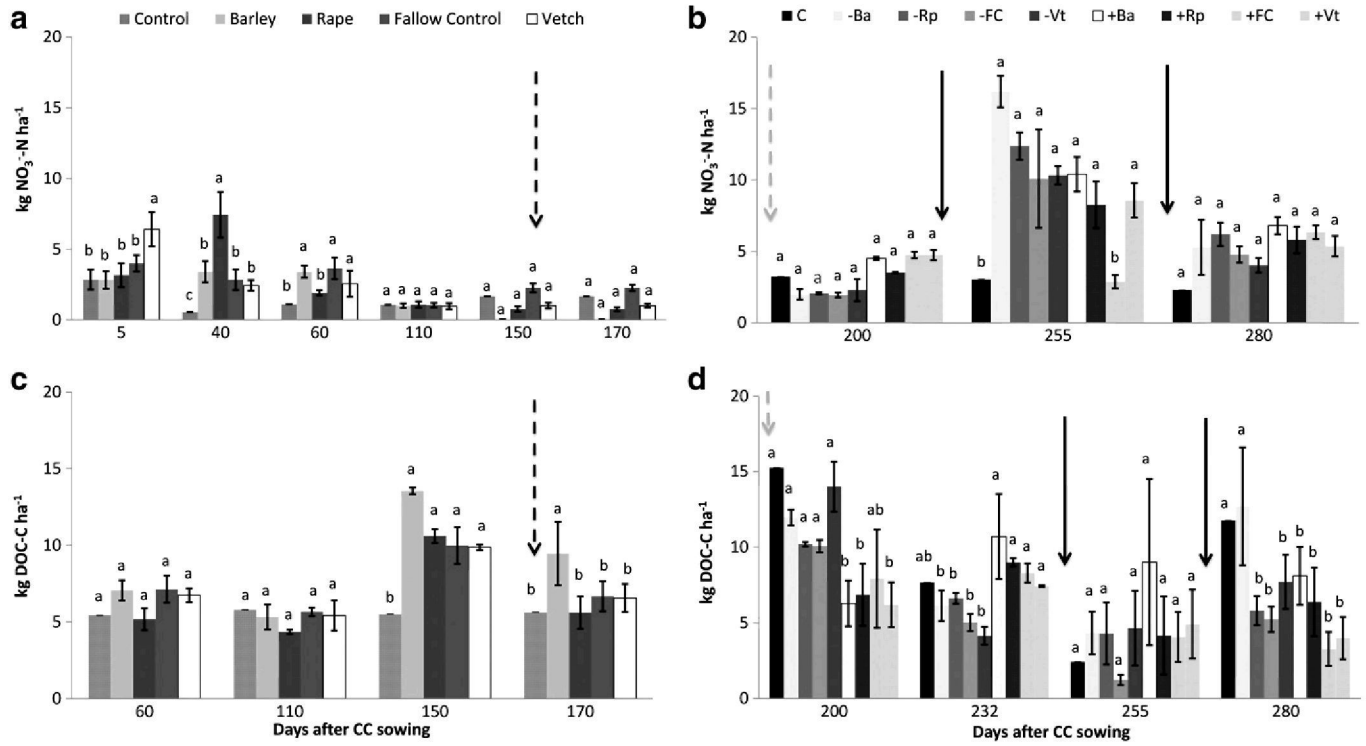

Fig. 3. Mean concentrations of NO_3^- (kg NO_3^-–N ha^{-1}) and DOC (kg DOC–C ha^{-1}) for each treatment in the fallow (a, c) and maize periods (b, d). The black bold arrows indicate the time of fertilizer application in the maize crop period. The dotted arrows indicate the CC harvest (black) and maize sowing (gray). Different letters over the bars indicate significant differences for that date by applying the Least Significant Difference (LSD) test at $P < 0.05$ (n = 3).

between 6.82 and 2.31 kg NO_3^-–N ha^{-1} 280 DAS (Fig. 3b). The nitrate concentration evolved similarly when the green manure was incorporated. However, the increase measured after the 1st fertilization was lower for +Ba and +Rp, with concentrations 36 and 33% lower than in −Ba and −Rp, respectively. Similarly, the NO_3^- concentration in +Rp and +F was 15 and 16% lower than in −Rp and −F, respectively. None of these differences was significant ($P > 0.05$). The incorporation of CC residues decreased the mean concentration of NO_3^- by 40%. No significant ($P > 0.05$) differences were measured between the treatments, except for +F and FC, which displayed significantly lower concentrations at 255 DAS.

The concentration of DOC was significantly ($P < 0.05$) lowered by the incorporation of green manure in all cases (2–22% decrease) at 200 DAS. The opposite occurred 32 days later (Fig. 3d), with the highest DOC concentration measured in the plots with CC residues incorporated (i.e., 232 DAS). Then, a decrease to values lower than 5 kg C ha^{-1} was observed in all cases except for +Ba. No significant ($P > 0.05$) differences were observed between CC from 255 DAS until the end of the experiment (i.e., 280 DAS). The only exceptions were for −Ba and FC, which displayed an increase of 66% in that period (Fig. 3d).

3.4.3. GHG fluxes

The incorporation of CC residues enhanced N_2O emissions in all cases except +Vt and +F, although the differences between the treatments were not significant ($P > 0.05$) (Table 2). Nitrous oxide emissions were driven by N application (Fig. 5a). Nitrogen application-increased emissions of N_2O, on average, 75 and 72% in plots with and without residues incorporated, respectively (Table 2). The N_2O fluxes were very low in the month preceding the 1st fertilization of maize, ranging from −7.51 to 3.31 g N_2O–N ha^{-1} d^{-1} for −Ba and −Vt, respectively (Fig. 5a, b). Two peaks were measured in the days following the 140 and 70 kg N ha^{-1} fertilization (DAF^{140} and DAF^{70}, respectively), as ammonium nitrate (AN) (Fig. 5a, b). The highest flux was measured at 9 DAF^{140} in the +Ba plots and was 54% higher than in −Ba. For the +Rp plots, the largest daily emission was observed at 1 DAF^{70}, being 50% higher than in −Rp. Negative fluxes were measured for +Vt, both when starting the measurements and at the conclusion of the measurements (Fig. 5b). The highest cumulative emissions were measured in +Ba and +Rp, and no significant differences ($P > 0.05$) were observed between them (Table 2). As occurred in the fallow period, the daily fluxes of N_2O were positively correlated ($P < 0.05$) with NO_3^- and negatively correlated with DOC concentration and drainage.

The incorporation of CC residues did not significantly affect CO_2 fluxes. In plots without incorporated plant residues, −Rp and −Vt were the treatments displaying the highest fluxes at 2 DAF^{70} (Fig. 5c). Thereafter, and until the last measurements, the daily losses of CO_2 were, although lower, significantly higher ($P < 0.05$) than before the sowing of maize and early stages of growth. The incorporation of Rp and Ba residues produced the largest CO_2 emissions but without significant differences ($P > 0.05$) between them and the other treatments (Table 2).

Methane fluxes fluctuated along the maize crop period (Fig. 5e, f). Both the lowest and highest fluxes were measured in the −Ba plots (Fig. 5e, f). More than 50% of the sampling days displayed negative fluxes in all cases, accounting for 72% in the −F plots. In plots with CC residues incorporated, +F, +Rp and +Ba displayed negative fluxes on 71, 72 and 50% of the sampling dates (Fig. 5f). This resulted in negative cumulative fluxes for all treatments but the FC and −Rp plots. In the case of the latter, the fluxes were 73% higher than in the +Rp plots. No significant differences were observed between treatments ($P > 0.05$) (Table 2). The incorporation of Vt and Rp residues produced the lowest and highest N_2O yield scaled emissions, respectively (1.11 ± 0.11 and 2.91 ± 0.32 g N_2O–N kg N $uptake^{-1}$, respectively) (Table 2).

4. Discussion

To date, few studies have focused on the effect of CCs on GHG fluxes in agricultural soils. These studies have mostly been focused

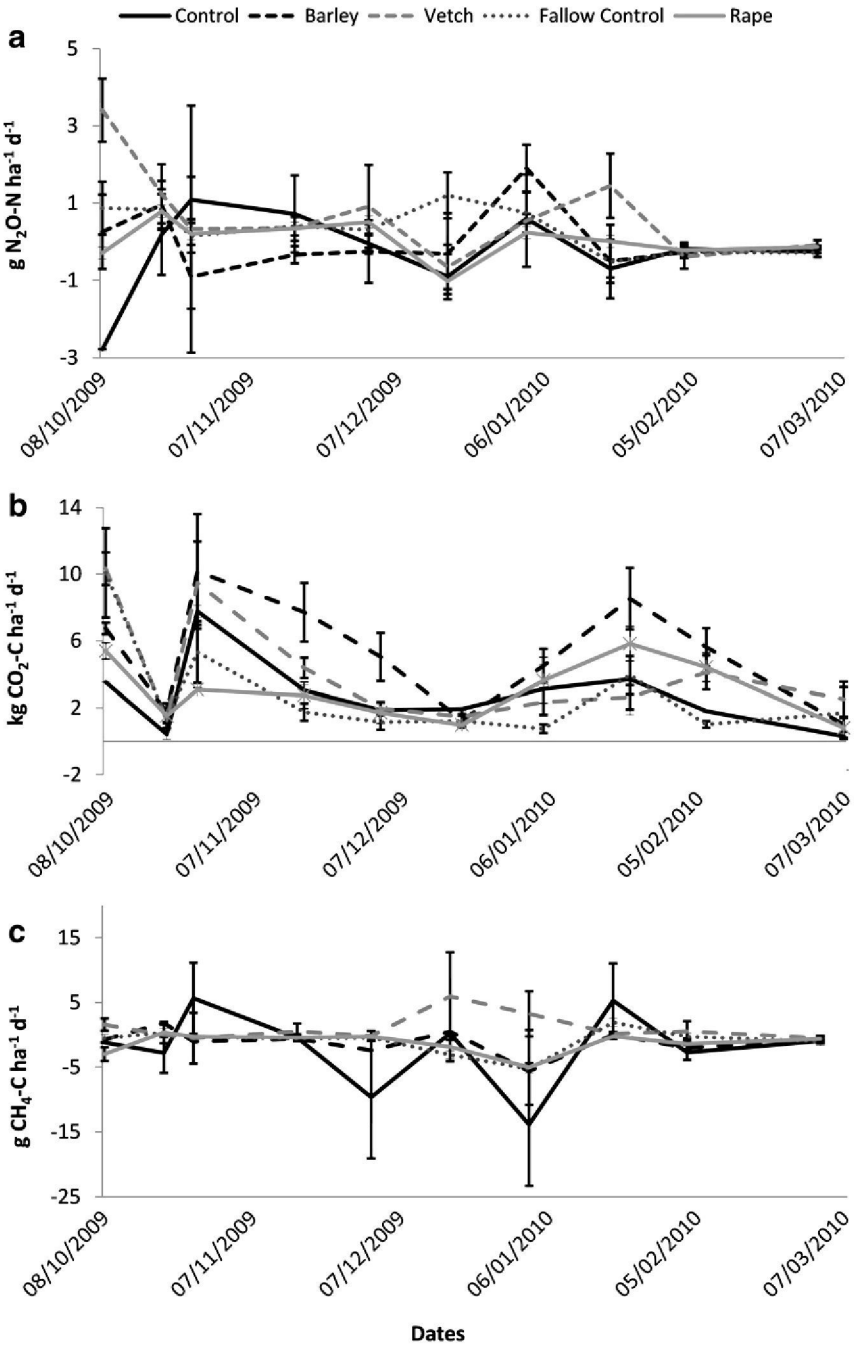

Fig. 4. Daily emissions of N_2O (g N_2O–N ha^{-1} d^{-1}) (a), CO_2 (kg CO_2–C ha^{-1} d^{-1}) (b) and CH_4 (g CH_4–C ha^{-1} d^{-1}) (c) in the fallow period. The vertical bars indicate the standard errors (n = 6).

on N_2O emissions from legume–cereal rotations in temperate areas, which display little influence of CCs on these fluxes (Baggs et al., 2000; van der Weerden et al., 2000; Pappa et al., 2011; Abdalla et al., 2012). In this context, Pappa et al. (2011) evaluated the effect of cereal legume intercropping (barley/pea) on N_2O losses in the north of Scotland and observed contrasting results depending on the barley/pea cultivar chosen. Only Chirinda et al. (2010) have assessed the effect of CCs (i.e., mostly legumes) on both N_2O emission and soil respiration (i.e., CO_2 fluxes) from several organic cropping systems differently managed in a temperate area (i.e., Denmark). These authors observed significantly increased CO_2 fluxes due to both the presence of CCs (i.e., perennial ryegrass and mixtures of perennial ryegrass, chicory and clover species) and its incorporation as green manure in the forthcoming winter wheat crop. The presence of CCs did not significantly affect N_2O fluxes in this study. As occurred in these regions, the use of CCs has also been proposed as an effective strategy to abate N losses in the form of leached NO_3^- in irrigated crops of semiarid Mediterranean areas (e.g., Gabriel et al., 2010, 2012). However, this study was the first attempt to simultaneously assess the influence of three different types of CC (i.e., legume, cereal and crucifer) on the direct GHG emissions of these systems, both during the fallow (using CCs as catch crops) and the maize crop period (using CCs residues as green manure).

4.1. Role of CC as catch crops: effect on the GHG losses in the CC period

The absence of N fertilization in this period justified the low N_2O fluxes measured in the three CC (Table 2). Vetch was the only CC

Table 2
Cumulative N_2O (g N_2O–N ha^{-1}), CO_2 (kg CO_2–C ha^{-1}) and CH_4 (kg CH_4–C ha^{-1}) emissions and yield (of maize) scaled N_2O emissions for all CC in the fallow and maize crop periods. Different letters within the columns indicate significant differences according to the Least Significant Difference (LSD) test at $P < 0.05$.

		N_2O (g N_2O–N ha^{-1})	CO_2 (kg CO_2–C ha^{-1})	CH_4 (kg CH_4–C ha^{-1})	Yield scaled N_2O (g N_2O–N kg N $uptake^{-1}$)
Fallow period	Vt	160.12 ± 19.98[a]	545.41 ± 46.41[b]	0.17 ± 0.17	–
	Ba	0.02 ± 10.11[b]	785.67 ± 112.51[a]	−0.19 ± 0.21	–
	Rp	0.01 ± 19.99[b]	440.91 ± 41.62[bc]	−0.18 ± 0.09	–
	F	40.21 ± 20.33[b]	342.82 ± 46.76[c]	−0.15 ± 0.18	–
	FC	−10.10 ± 10.42[b]	413.73 ± 80.21[bc]	−0.27 ± 0.17	–
Maize crop period	−Vt	170.09 ± 90.32	1408.52 ± 283.71	−0.21 ± 0.13	2.21 ± 0.15
	−Ba	160.44 ± 30.41	1306.65 ± 259.42	−0.03 ± 0.15	1.55 ± 0.39
	−Rp	240.08 ± 9.99	1246.41 ± 287.81	0.05 ± 0.03	2.14 ± 0.13
	−F	170.11 ± 120.12	1118.72 ± 382.91	−0.20 ± 0.06	2.93 ± 1.89
	FC	60.05 ± 30.31	1009.72 ± 110.13	0.05 ± 0.08	2.22 ± 0.36
	+Vt	130.15 ± 10.12	1318.18 ± 415.32	−0.20 ± 0.19	1.09 ± 0.11
	+Ba	270.11 ± 160.09	1657.91 ± 450.84	−0.01 ± 0.08	2.35 ± 1.86
	+Rp	290.52 ± 300.01	1736.52 ± 133.11	−0.12 ± 0.12	2.95 ± 0.29
	+F	120.03 ± 89.98	1193.43 ± 672.92	−0.19 ± 0.13	2.16 ± 0.94
	ANOVA	NS	NS	NS	NS

significantly affecting N_2O emissions, producing a 4-fold increase with respect to F (Table 2). The largest fluxes of N_2O occurred immediately after the sowing of Vt (Fig. 3a), which might be related to the presence of residual mineral N from previous crops. This would be in accordance with the significantly highest NO_3^- concentration measured in the Vt plots 1–3 weeks after sowing (i.e., 41, 40, 51 and 37% higher than in FC, Ba, Rp and F, respectively, 5 DAS) (Fig. 3a). Thereafter (>30 DAS), the NO_3^- concentration decreased below 3.72 kg N ha^{-1}, most likely as a consequence of N leaching and uptake by the crop, and the differences in fluxes between the treatments were not significant. In contrast with our initial hypothesis, the N_2O flux was similar for F, Ba and Rp. The expected decrease in the pool of NO_3^-, associated to a higher N uptake of these CCs, was not observed in the upper part of the soil or in the measured fluxes. Frequent rainfall in this period may have promoted NO_3^- leaching, maintaining the observed low concentration of soil mineral N (Fig. 3a), independently of the CC presence. Because the WFPS of soils was maintained above 55% for many dates, especially in the F plots, the coexistence of aerobic and anaerobic microsites was expected to occur (Mathieu et al., 2006). Although under these moisture conditions, nitrification and denitrification processes generally coexist in soils, the positive correlation observed between NO_3^- and N_2O fluxes confirmed that denitrification was an important process in the production of N_2O in this soil. In addition, the negative fluxes measured at some sampling dates also indicated a simultaneous consumption of N_2O through complete denitrification. This sink effect for N_2O has been described in other cropping systems (e.g., Højberg at al., 1994; Chapuis-Lardy et al., 2007; Abalos et al., 2012), especially under conditions of low NO_3^- concentrations in the soil. In these situations, denitrifiers can use N_2O as an electron acceptor, thus reducing it to N_2. In this experiment, the highest frequency of dates with negative fluxes was observed for Ba (70% of sampling dates), which could have been associated with the low level of NO_3^- in these plots (<0.42 kg N ha^{-1}) in an important part of the period (Fig. 3a).

The presence of CC significantly reduced the WFPS in comparison to F, but a clear effect over N_2O fluxes, associated with soil moisture, was not detected. In addition, the high CO_2 emissions from CC plots may indicate both important respiration and metabolic activity in the rhizosphere (Fig. 4b). This may have promoted the consumption of O_2 and anaerobic conditions suitable for denitrification (Drury et al., 1991). The low concentration of NH_4^+ in the soil throughout this fallow period also contributed to limiting the weight of nitrification in N_2O fluxes in comparison with denitrification.

Carbon dioxide fluxes were increased by CC in all cases, although only Vt and Ba produced significant differences compared with F (26 and 44% increase, respectively). These differences were related to the CC biomass because plants were included inside the chambers during the GHG measurements of this period. Vetch and Ba were the CCs presenting the highest biomass values (Table 1). Therefore, larger CO_2 fluxes might have been highly associated to plant respiration.

Methane fluxes were negative in all cases but Vt, although no significant differences ($P > 0.05$) were observed between the treatments. There is evidence in the literature that after the addition of N fertilizers, including NH_4^+- or NH_4^+-generating compounds, the oxidation capacity of the soil can be reduced (Steudler et al., 1989; Hütsch et al., 1996). This has been explained as a result of an inhibitory effect of NH_4^+ at the cellular level due to competitive inhibition of the enzyme responsible for the oxidation of CH_4 (CH_4 monooxygenase) with the NH_3 monooxygenase (Dunfield and Knowles, 1995; Le Mer and Roger, 2001). In our case, as no N fertilizer was applied at this stage of the study, this potential effect was not expected to occur. Nevertheless, the observed effect of Vt decreasing CH_4 fluxes could have been related to the higher mineral N of these plots, possibly as a result of the mineralization of N-rich plant material from previous years (Gabriel et al., 2012).

4.2. Role of CC as green manure: influence over the GHG emission in the maize cropping system

4.2.1. GHG fluxes prior N fertilization

Initially, the incorporation of green manure produced contrasting effects on the mineral N and DOC of the upper soil (Fig. 3) but not on GHG emissions. The nitrate concentration was slightly increased as a consequence of the incorporation of residues, most likely because the more labile organic fractions were mineralized in this short period of time (Baggs et al., 2000). However, the frequent rainfall promoted drainage and maintained NO_3^- concentration below 4.73 kg N ha^{-1} in all treatments. The dissolved organic C of the soil was also affected by incorporation of residues, with a significant reduction compared with no addition in the 10 days following incorporation and a significant increase after 40 days.

Nitrous oxide fluxes were low along this period for all CCs, even negative in some cases (Fig. 5a). These results could be explained by a combination of a low NO_3^- concentration and suitable environmental and soil conditions for completed denitrification (e.g., WFPS ≥60%; soil temperature ≥20 °C). The high pH of soil (8.23) also favored complete denitrification (Šimek and Cooper, 2002). The scarce influence of residue composition on WFPS, DOC and soil NO_3^- justified the similar GHG fluxes measured in all treatments along this period (April–May) (Fig. 5).

4.2.2. GHG emissions following N fertilization

Nitrogen fertilization was the main factor driving N_2O emissions in this period (Fig. 5a). This finding is in accordance with previous

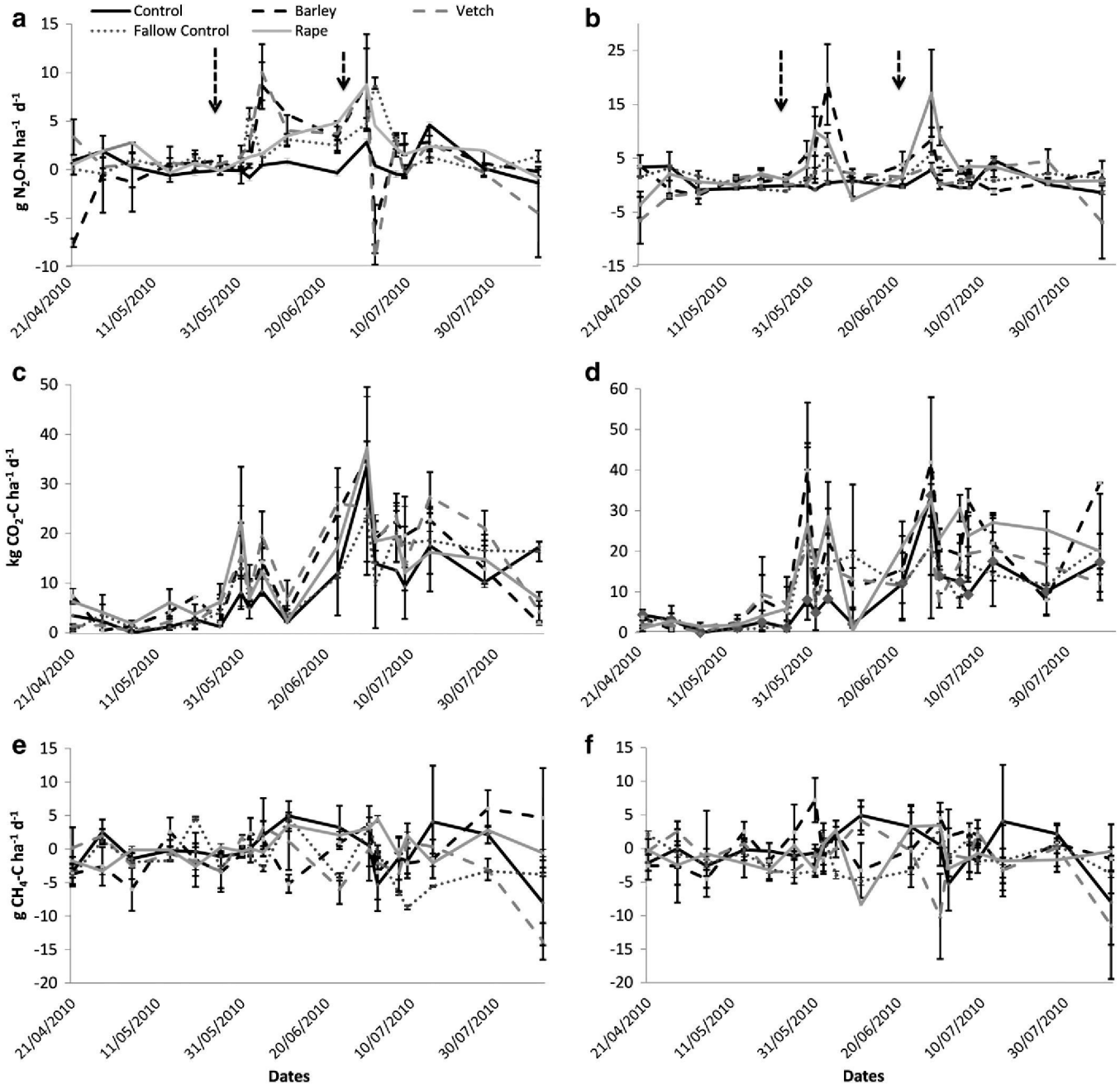

Fig. 5. Daily fluxes of N_2O (g N_2O–N ha^{-1} d^{-1}) (a, b), CO_2 (kg CO_2–C ha^{-1} d^{-1}) (c, d) and CH_4 (g CH_4–C ha^{-1} d^{-1}) (e, f) in the maize period. The fluxes from plots where CC residues were incorporated (on the right: b, d, f) and not incorporated (on the left: a, c, e) are shown. The arrows represent the application of N fertilizer as AN (140 and 70 kg N ha^{-1}). The vertical bars indicate the standard errors (n = 3).

research, where increased N_2O fluxes have been measured after N fertilization (e.g., Stehfest and Bouwman, 2006). Fertilization increased the concentration of mineral N (Fig. 3), thus promoting suitable conditions for N_2O production through both nitrification and denitrification. The mean soil moisture increased in the 2 weeks following the two fertilizer applications (averaging 63, 70, 71% WFPS for +Ba, +Rp and +Vt, respectively) due to both irrigation and rainfall (Fig. 2a, b). Under these conditions, the coexistence of nitrification and denitrification was expected to occur in unsaturated soils (i.e., WFPS ≤70%). Mathieu et al. (2006) suggested that under these conditions, c. 60% of N_2O is originated through nitrification. Based on this, nitrification is the most likely mechanism responsible for N_2O production in the first 15 DAF^{140}, mainly in the +Ba plots where the highest N_2O emission levels were measured at that time (Fig. 4b). The ammonium fraction of the fertilizer would have been oxidized, thus increasing soil NO_3^- concentration up to a maximum 20 DAF^{140} (Fig. 3b). These results are in accordance with Sanz-Cobena et al. (2012), who measured an increase in N_2O fluxes from nitrification 12 days after N fertilization in an irrigated maize crop. Because WFPS was kept above 55%, denitrification was most likely enhanced at anaerobic microsites, which also contributed to the N_2O fluxes in this period (Peoples et al., 2004; Stehfest and Bouwman, 2006). In the case of the +Ba and +Rp plots, the combination of a high C:N ratio with the addition of an external source of mineral N increased fluxes of N_2O in comparison with −Ba and −Rp. This has been observed elsewhere by Abalos et al. (2012) when maize straw (C:N > 30) was incorporated in the soil in autumn. They observed the largest effect of interaction between residues and N fertilizer

4–6 months after application and explained the results as increased microbial activity due to the confluence of soluble C and N sources. In our experiment, the N_2O fluxes were higher for 2–4 months after incorporation (Fig. 5). The higher soil moisture and soil temperature combined with the incorporation of crop residues with lower C:N ratio than those used by Abalos et al. (2012) explain these temporal effect differences.

The incorporation of CC residues reduced NO_3^- concentration at this time of the study. Although differences between treatments were not significant, this decrease may have been associated to an immobilization effect of the plant material over mineral N. This was mainly observed in the +Ba plots due to the higher C:N ratio of this organic residues. It has been observed that the incorporation of plant residues with C:N ratios higher than 18, such as these of cereals, enhances N immobilization (Abalos et al., 2012). The application of a lower amount of N (70 kg N ha^{-1}), the N uptake by the maize plants at the maturity stage (i.e., 65 days after sowing) and increased N leaching due to irrigation may explain the lower amount of NO_3^- measured following the 2nd fertilization (Fig. 2b).

According to the observed high soil respiration rates (Fig. 5c, d), N application may have also increased both the heterotrophic activity of soil microbiota and the growth of the maize rooting system, resulting in a growth in CO_2 fluxes (e.g., Mendoza et al., 2006; Ramirez et al., 2010). These results agree with the results of Chirinda et al. (2010), who observed a 30% increase in CO_2 fluxes due to the incorporation of CC residues in crop rotation. These authors argued that this was associated with a general increase of C inputs, microbial biomass and activity. In the case of N-rich CC (i.e., legumes), they also considered enhanced N availability as an important factor behind the growing microbial activity and soil respiration rates. Meijide et al. (2009) also observed this increasing effect of N fertilization over CO_2 fluxes in semiarid soil sown with barley. The cumulative emissions of CO_2 were in the range of other studies conducted in soils treated with synthetic N fertilizers (Abalos et al., 2012), being higher than 1000 kg CO_2–C ha^{-1} in all fertilized plots. Considering the total experimental period (fallow + maize crop), a CH_4 sink effect was measured in all cases. However, −Vz and +Vz were the treatments with a significant lower oxidation capacity (−0.03 and −0.04 kg CH_4–C ha^{-1}). Nitrogen fertilization may have decreased the oxidation capacity of the soil (Steudler et al., 1989; Hütsch et al., 1996) due to an inhibitory effect of NH_4^+, resulting in competitive inhibition between the enzymes participating in the oxidation of CH_4 and nitrification (Dunfield and Knowles, 1995; Le Mer and Roger, 2001).

The calculated direct N_2O EF during the experimental period for plots with and without incorporated CC residues was 0.12 ± 0.03 and 0.10 ± 0.01%, respectively. This is lower than the IPCC EF for synthetic fertilizers (1.00; IPCC, 2007) and the values proposed by other authors in similar cropping systems fertilized with AN (1.8–2.2 EF, Dambreville et al., 2008). When taking into account the N content of incorporated residues, the +Vt plots displayed the lowest EF (0.03 ± 0.01%) in the maize crop period. However, when considering emissions for the entire experiment, this value increased up to 0.09 ± 0.01%, which was similar to the values for +Ba and +Rp (0.08 ± 0.02 and 0.09 ± 0.01%, respectively). The emission factors were low due to a decreased NO_3^- concentration as a result of 1) hypothesized complete denitrification of NO_3^- to N_2 (Rochester, 2003); 2) NO_3^- leaching, which was expected to be high according to drainage data (Figs. 1b) and 3) crop uptake. Unlike Gabriel et al. (2012), the irrigation was not adjusted to crop requirements but was applied following the standard farming practices in the region (700–800 mm). This resulted in a total volume of drained water of 241 mm in the crop period, 40% of which occurred in the month following fertilization.

Scaling these results to agronomic parameters (e.g., N uptake by grain) allowed us to propose CC-specific management practices to abate GHG emissions in this type of cropping systems. Based on this, the yield-scaled N_2O emissions were only decreased by the incorporation of Vt residues. Nevertheless, there were no significant differences between the treatments in the crop period. Taking into account that the use of CC has been shown to be an useful strategy to mitigate N losses by reducing NO_3^- leaching (Gabriel et al., 2012), their contribution to reducing indirect N_2O emission, especially in regard to NO_3^- leaching (Aguilera et al., 2013), is expected to be high, thus constituting a great opportunity for N_2O mitigation. In this context, further field research simultaneously assessing the impact of CC on direct and indirect N_2O emissions is necessary to verify the results of previous studies. In addition, due to the scarcity of studies on GHG from crop rotations with CC under semiarid conditions, a larger number of studies would allow generalization of the results of this study.

5. Conclusions

The use of CC in agricultural systems can be considered a good strategy to decrease N losses in both crop (CC residues used as green manures) and intercrop periods (CCs used as catch crops). The type and characteristics of the CCs influenced their efficiency at affecting water availability, N and C pools and the processes leading to GHG emissions. Vetch was the only CC that significantly enhanced N_2O losses in the intercrop period, mainly due to the N remaining in these plots from the sowing of previous crops. Although WFPS ranged from 40 to 65%, the emitted N_2O was mainly produced through denitrification. The low nitrate concentration in soil, which was highly affected by the N uptake performed by the catch crops and the N lost through leaching, explained the low, and often negative, fluxes observed throughout the CC period for all treatments. N_2O emissions were lower than expected in the fertilized maize crop, which was also characterized by soil conditions favoring denitrification. The incorporation of CC as green manure had a significant influence over N_2O fluxes in the 2–4 month period following the application of CC residues in the +Rp and +Ba treatments. This was associated to the interaction of CC residue and the N fertilizer application. Barley residue, with the highest C:N ratio (18), produced the largest increase (1.71-fold) in total N_2O fluxes. The CO_2 fluxes were significantly increased by the presence of CC, both in the fallow and maize periods. The incorporation of residues from Ba and Rp in soil significantly increased these fluxes in the maize crop period. Considering the total experimental period (fallow + maize crop), a CH_4 sink effect was measured in all cases. However, −Vz and +Vz were the treatments with a significantly lower oxidation capacity. No effects of CC residue incorporation on total CH_4 were measured. To obtain more complete information about the potential of CC as a GHG mitigation strategy, indirect N_2O emission associated to NO_3^- leaching must also be considered. Given the already known abating effect of CC on N leaching, the possibility for overall mitigation appears to be high.

Acknowledgments

The authors are grateful for the financial support received through project awards from the Spanish Ministry of Science and Innovation (AGL2009-08412-AGR), the Community of Madrid (Agrisost Project, S2009/AGR-1630) and the Académie universitaire Louvain, co-funded by Marie Curie actions of the EU, FSR 2012 (SPER/DST/340-1120525). Finally, this study would not have been possible without technical assistance from the technicians at the Departments of Chemistry and Agricultural Analysis and Vegetal Production of the Agronomy Faculty (Technical University of Madrid, UPM). We offer a special thanks to the technicians working with us at the "La Chimenea" field station (IMIDRA).

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